

# Highly efficient and selective oxidation of secondary alcohols to ketones under organic solvent and transition metal free conditions

Suman L. Jain, Vishal B. Sharma and Bir Sain\*

Chemical and Biotechnology Division, Indian Institute of Petroleum, Dehradun-248005, India

Received 3 February 2006; revised 15 April 2006; accepted 28 April 2006

Available online 24 May 2006

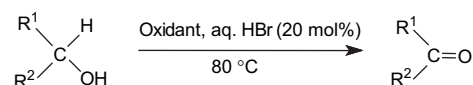
**Abstract**—The aqueous HBr/H<sub>2</sub>O<sub>2</sub> was found to be highly efficient and green catalytic system for the selective oxidation of the secondary alcohols to ketones in excellent yields under organic solvent free conditions. The results of the oxidation of the secondary alcohols with solid alternatives of the aqueous hydrogen peroxide like SPC or SPB are also described.

© 2006 Elsevier Ltd. All rights reserved.

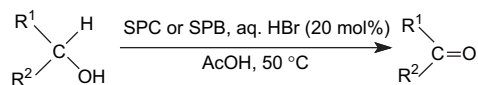
## 1. Introduction

The development of catalytic synthetic methodologies using clean oxidants like molecular oxygen and hydrogen peroxide with a view to replace environmentally prohibitive stoichiometric oxidants is an area of current interest.<sup>1</sup> Hydrogen peroxide is an attractive, atom-economic, and environmentally benign oxidant as it is cheap, easily available, and produces only water as by-product. In the recent years, it has been extensively used in developing a variety of synthetically important oxidation methodologies like epoxidation, oxidation of alcohols, aldehydes, and sulfides using transition metal based catalysts both in homogeneous and heterogeneous phases.<sup>2</sup> The oxidation of secondary alcohols to carbonyl compounds is an important synthetic transformation<sup>1a,3</sup> and a variety of transition metal based catalysts, such as methyltrioxorhenium<sup>4</sup> dinuclear iron complexes,<sup>5</sup> vanadium phosphorus oxide,<sup>6</sup> cobalt(II) complexes,<sup>7</sup> Fe<sup>3+</sup>/montmorillonite-K10 system,<sup>8</sup> and sodium tungstate<sup>9</sup> using hydrogen peroxide as oxidant, have been reported in the literature to accomplish it. However, most of these methods are associated with the limitations such as use of toxic, expensive metals, lower yields of the products, and oxidation of only activated such as benzylic and allylic alcohols. In the recent past, increasing emphasis is being placed toward the development of transition metal free ecofriendly synthetic methodologies to avoid the use of toxic and expensive metals and their complexes. In our preliminary communication,<sup>10</sup> we have reported a new and highly efficient methodology for the oxidation of secondary alcohols to ketones with aqueous H<sub>2</sub>O<sub>2</sub> in the presence of catalytic amounts of HBr

under very mild conditions. Our further observation that this system works more efficiently under organic solvent free conditions prompted us to describe the full details of this improved protocol along with the applications of solid oxidants in the place of aqueous hydrogen peroxide (Schemes 1 and 2).



Scheme 1.



Scheme 2.

## 2. Results and discussion

The oxidation of various secondary alcohols, both activated and non-activated, was carried out by heating the reaction mixture of substrate (1 mmol), aqueous 30 wt % hydrogen peroxide (2 mmol), and catalytic amount of aqueous HBr (20 mol %) at 80 °C under organic solvent free conditions. All the alcohols were selectively converted to the corresponding ketones in excellent yields and these results are presented in Table 1. Among the various alcohols studied, benzoin was found to be the most reactive and required shorter reaction times for their oxidation (Table 1, entries 17 and 18). Furthermore, aromatic substituted alcohols were found to be more reactive than aliphatic/alicyclic (Table 1, entries 1 and 2). Alcohols having both secondary

**Keywords:** Oxidation; Secondary alcohols; Ketones; Solid oxidant.

\* Corresponding author. Tel.: +91 135 2660071; fax: +91 135 2660202; e-mail: [birsain@iip.res.in](mailto:birsain@iip.res.in)

**Table 1.** Oxidation of secondary alcohols to ketones

Entry	Substrate	Product	Method A		Method B	
			Reaction time (h)	Yield <sup>a</sup>	Reaction time (h)	Yield <sup>a</sup>
1			0.50	98	1.0	96
2			0.75	94	1.0	90
3			2.0	89	2.0	80
4			3.5	75	3.0	72
5	$\text{CH}_3(\text{CH}_2)_4\text{C}(\text{OH})\text{C}\equiv\text{CH}$	$\text{CH}_3(\text{CH}_2)_4\text{C}(=\text{O})\text{C}\equiv\text{CH}$	5.00	82	5.5	75
6			4.50	76	4.0	70
7			2.5	85	3.5	82
8			1.75	82	2.0	80
9			2.0	89	2.5	86
10			2.0	87	2.75	84
11			1.5	82	2.5	80
12			3.5	75	4.0	70
13			2.75	85	3.5	82

(continued)

Download English Version:

<https://daneshyari.com/en/article/5227380>

Download Persian Version:

<https://daneshyari.com/article/5227380>

[Daneshyari.com](https://daneshyari.com)